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# **Overcoming chemical equilibrium limitations using a thermodynamically reversible chemical reactor**

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**All real processes be they chemical, mechanical or electrical, are thermodynamically irreversible and therefore suffer from thermodynamic losses. Here, we report the design and operation of a chemical reactor capable of approaching thermodynamically-reversible operation. The reactor was employed for hydrogen production via the water-gas shift reaction, an important route to ‘green’ hydrogen. The reactor avoids mixing reactant gases by transferring oxygen from the (oxidising) water stream to the (reducing) carbon monoxide stream via a solid-state oxygen reservoir consisting of a perovskite phase ( $\text{La}_{0.6}\text{Sr}_{0.4}\text{FeO}_{3-\delta}$ ). This reservoir is able to remain close to equilibrium with the reacting gas streams because of its variable degree of non-stoichiometry and thus develops a ‘chemical memory’ which we employ to approach reversibility. We demonstrate this memory using operando, spatially-resolved, real-time, high-resolution x-ray powder diffraction on a working reactor. The design leads to a reactor unconstrained by overall chemical equilibrium limitations, which can produce essentially pure hydrogen and carbon dioxide as separate product streams.**

26 Reducing thermodynamic losses within the chemical industry has driven the design of highly  
27 efficient heat and mass transfer devices as well as the methodologies to enable such design<sup>1</sup>.  
28 However, the heart of any chemical process, the chemical transformation occurring within the  
29 reactor, has not yet received the same level of attention; there is currently no recipe for  
30 producing a thermodynamically reversible chemical reactor and most reactors manifest very  
31 significant irreversibilities<sup>2</sup>. Here we design and operate such a thermodynamically  
32 reversible reactor. One impact of the reactor is its ability to overcome overall reaction  
33 equilibrium limitations. This property is significant as many chemical reactions are  
34 reversible in nature and their conversions are limited by reaction equilibrium. Such  
35 limitations leads to incomplete conversion of reactants, which then exit the reactor mixed  
36 with the products. This results in enormous cost to the chemical industry which must design  
37 and operate complex separation schemes to purify products. Although Dudukovic<sup>3</sup> identifies  
38 combining reaction and separation as a key means of avoiding such equilibrium constraints,  
39 there have, until now, been no ways of avoiding equilibrium constraints without the need for  
40 a simultaneous separation.

41 Chemical transformations are conventionally performed via ‘mixed’ reactions.  
42 Multiple reactants, initially separate, are mixed, the reaction mixture is heated to the reaction  
43 temperature and the reaction is allowed to proceed. The very act of mixing results in  
44 significant thermodynamic losses (one will inevitably need to expend energy to separate the  
45 reactants and the individual products). It is, however, possible to avoid mixing using a  
46 dynamic approach often referred to as chemical looping<sup>4-7</sup>. Indeed some of the potential  
47 thermodynamic advantages of such an approach have been recognised for e.g. combustion  
48 processes<sup>8,9</sup>. There has, however, been no recognition of how a dynamic or ‘unmixed’  
49 approach could be used to overcome overall reaction equilibrium constraints.

50 Here we consider the reversible water-gas shift (WGS) reaction,

51



53

54 where  $\text{H}_2\text{O}$  is reacted with  $\text{CO}$  to produce  $\text{H}_2$  and  $\text{CO}_2$ . Reaction 1 is key to many  $\text{H}_2$   
55 production processes and performed on a very large scale industrially (total capacity of 50  
56 million tons per annum<sup>10</sup>). The reaction is equilibrium limited (Fig. 1a and Supplementary  
57 Video 1; a high-resolution version of the video can also be found at  
58 <http://nuvision.ncl.ac.uk/Play/18143>) and this leads to significant process complexity  
59 involving multiple reaction stages and separation. Overcoming this equilibrium limitation  
60 through the use of membranes<sup>11-13</sup> and  $\text{CO}_2$  absorption<sup>14-19</sup> has attracted considerable  
61 attention in the past. In a chemical-looping WGS reactor,  $\text{H}_2\text{O}$  (high oxidising potential) is  
62 first passed over a solid phase carrier of oxygen (oxygen carrier material or OCM) that  
63 accepts oxygen resulting in the production of  $\text{H}_2$ . Then in a second step  $\text{CO}$  (low oxidising  
64 potential) is passed over the solid phase, removing oxygen to produce  $\text{CO}_2$ .

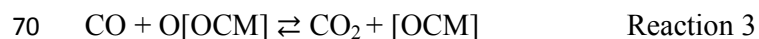
65

66 Step 1,  $\text{H}_2\text{O}$ -feed, bed-oxidation half cycle:



68

69 Step 2,  $\text{CO}$ -feed, bed-reduction half cycle:



71

72 Thus we avoid gas-phase mixing of the  $\text{H}_2\text{O}$  and  $\text{CO}$  reactants and exploit the fact that the  
73 WGS reaction is an oxygen transfer reaction by performing the transfer in two separate steps

74 (a H<sub>2</sub>O-feed, bed-oxidation half cycle and CO-feed, bed-reduction half cycle) through the use  
75 of an OCM. The conversion to products is then no longer limited by the chemical  
76 equilibrium of Reaction 1 but rather by the individual equilibria associated with Reactions 2  
77 and 3. Conventional OCMs, such as metal-metal oxides, function by donating oxygen and  
78 receiving oxygen, at the fixed oxygen chemical potentials associated with their phase  
79 transitions (Fig. 1b). The practical consequence of this is that one can never have an OCM  
80 that gives a high conversion for both Reaction 2 and Reaction 3 at the same time (Fig. 1c and  
81 1d). The chemical-looping reactor's operation is also compromised thermodynamically  
82 because the driving force for oxygen exchange between gas and solid can never be  
83 vanishingly small. This is because the oxygen resides in the solid at a fixed oxygen chemical  
84 potential, whereas in the gas phase, there is a variable oxygen chemical potential as the gas  
85 composition must, for any reasonable conversion, change significantly between reactor inlet  
86 and outlet. In fact by some measures such a reactor can perform no better than a  
87 conventional 'mixed' reactor (Supplementary Video 1 and Supplementary Information  
88 Section 2).

89         An alternative way of viewing the process is that the OCM is required to transfer  
90 chemical information between the H<sub>2</sub>O-feed half cycle and CO-feed half cycle for the reactor  
91 to operate. A conventional metal-metal oxide system involving a single phase transition  
92 (between metal and metal oxide) stores no information about the oxygen chemical potential  
93 of the gases to which it has been exposed other than they were sufficiently reducing or  
94 oxidising to cause the phase transition. So a single OCM does not have the chemical memory  
95 to transfer sufficient information (i.e., the full oxidising and reducing potential of feed gases)  
96 for the reactor to achieve high conversions in both half cycles. In theory, it would be possible  
97 to transfer more information between half cycles by using axially-separated OCMs with  
98 differing oxygen chemical potentials associated with their phase transitions and moving to a

reverse flow design (oxidising and reducing feeds are fed to opposite end of the reactor). The OCMs would need to be spatially arranged such that the most easily oxidised is at the end of the bed which is exposed to the oxidising feed and the most easily reduced at the reducing feed end. We show in the Supplementary Information that, for the WGS reaction at 820°C, if  $n$  phase transitions are available using a series of  $n$  conventional OCM materials, a maximum conversion of  $n/(n+1)$  can be achieved (Supplementary Information Section 2). Unfortunately, this approach, whilst an improvement, would require large numbers of different OCMs to achieve high conversions and would be inflexible if the redox ability of feeds and/or products were changed. If two phase transitions were available within a single material a further benefit can be gained<sup>20</sup> but the system would still lack the flexibility to respond to changing inlet redox abilities (full discussion in Supplementary Information Section 2).

Here we demonstrate that a ‘chemical memory reactor’ can be built using a single OCM capable of transferring the necessary information for thermodynamically reversible operation between the two half cycles. The OCM can only perform this function in the absence of mixing in the solid phase in order to allow spatially-resolved information to be stored, transferred between half cycles and subsequently read. The oxidising end of the bed must remember the oxygen chemical potential of the most oxidising gas it experiences and the reducing end must remember the oxygen chemical potential of the most reducing gas it experiences throughout the cycles. We therefore need an oxygen carrier that can support the full range of oxygen chemical potentials required (Figure 1e and 1f). This leads us to select an oxide of variable oxygen non-stoichiometry as OCM<sup>21,22</sup>, such OCMs having been used previously in chemical looping for kinetic or stability benefits<sup>23,24</sup>. In these materials we know that the oxygen content will be a continuous function of oxygen chemical potential (furthermore we employ oxidising and reducing streams that can exhibit defined oxygen

chemical potentials, here achieved by the presence of two distinct redox couples,  $\text{H}_2/\text{H}_2\text{O}$  and  $\text{CO}_2/\text{CO}$ ). To summarise, in order to transfer the chemical information required between half cycles, we must simultaneously use reverse flow (so that one end of the bed is always oxidised and the other always reduced), we must use a solid that can support the full range of oxygen chemical potentials required (so that its state can reflect that of the reactant streams) and we must use a solid phase held within a fixed bed (so that solid phase mixing does not result in loss of chemical information).

Our ‘chemical memory reactor’ then consists of a bed of a non-stoichiometric oxide OCM operated in reverse gas flow (Fig. 1e and 1f) which permits an extensive exchange of chemical information through the OCM between each half cycle. Repeated application of the oxidising feed to the oxidising end of the bed and the reducing feed to the reducing end of the bed causes an oxidation state profile to develop along the length of the bed (Fig. 1g and 1h and Supplementary Video 1). Provided each half cycle is short enough that we do not destroy this oxidation state profile (‘memory’), the bed will ‘remember’ the oxygen chemical potentials associated with its feed streams. The gradual oxidation state profile also leads to small thermodynamic driving forces for the reactions occurring at each point along the reactor’s length and it therefore approaches reversible operation. Whilst recognizing the constraint that the reducing product stream can be no more reducing than the reducing feed and the oxidising product stream no more oxidising than the oxidising feed, we may achieve arbitrarily high overall conversion of the individual Reactions 2 and 3 and hence the overall Reaction 1.

## Results

To prove both the concept and the mechanism, an unmixed water-gas shift reaction was performed in such a reverse-flow memory reactor with a non-stoichiometric LSF ( $\text{La}_{0.6}\text{Sr}_{0.4}\text{FeO}_{3-\delta}$ ) perovskite oxygen-carrier material (Supplementary Information Section 1). The nominal temperature of operation ( $820^\circ\text{C}$ ) was chosen such that the equilibrium constant for the conventional mixed water-gas shift reaction (Reaction 1),  $K$ , is unity (the measured temperature in the reactor ranges from  $790^\circ\text{C}$  to  $820^\circ\text{C}$  causing the equilibrium constant to vary between 1.12 and 1.01).  $\text{La}_{0.6}\text{Sr}_{0.4}\text{FeO}_{3-\delta}$  was judged to be appropriate for use at this temperature as it is known to be both oxygen non-stoichiometric and stable over a very large range of oxygen chemical potentials, and remains single phase throughout the temperature and oxygen partial pressure range of our experiments. At the temperature of operation, oxygen capacity comes from reduction of Fe(III) to Fe(II) accompanied by oxygen vacancy formation. Oxygen is able to rapidly enter and leave the OCM structure as a result of both high oxygen-ion and electron conductivity.

The reactor was housed in a custom-made furnace and operated at the high-resolution x-ray powder diffraction beam line (ID22) of the European Synchrotron Radiation Facility (ESRF). As an indicator that equilibrium has been overcome, we evaluate for each cycle a variable,  $K^*$  (Supplementary Information Section 2), which measures the reactor performance and is maximised for simultaneously high conversions to both  $\text{H}_2$  and  $\text{CO}_2$ ,

$$K^* = \frac{\bar{y}_{\text{H}_2}\bar{y}_{\text{CO}_2}}{\bar{y}_{\text{H}_2\text{O}}\bar{y}_{\text{CO}}} \quad \text{Equation 1}$$

where  $\bar{y}_i$  is a time-averaged mole fraction at the reactor outlet. For a conventional mixed-reactant reactor,  $K^*$  would never be able to exceed the water-gas-shift equilibrium constant,  $K$ , of unity. Practically this means that conversions to  $\text{H}_2$  and  $\text{CO}_2$  would not be able to



171 exceed 50% for a stoichiometric feed. Similarly, the  $n/(n+1)$  conversion limitation discussed  
172 above means that  $K^*$  can never exceed unity for an oxygen-carrier material with a single  
173 phase-transition such as that in Fig. 1c and 1d. Our non-stoichiometric oxide, however,  
174 behaves as if it supplies a very large number of phase transitions and thus there is no upper  
175 limit to the value of  $K^*$ . Experimentally, we observe  $K^*$  values much greater than unity  
176 when we operate our reactor as shown in Fig. 2a. As the bed used was prepared in an  
177 oxidised state, initial high conversions of CO to CO<sub>2</sub> are achieved with lower conversions of  
178 H<sub>2</sub>O to H<sub>2</sub> (Region A of Fig. 2a and Supplementary Fig. 7). After cycling, a profile of  
179 oxidation state of the material becomes established and each cycle becomes repeatable with  
180 conversions of H<sub>2</sub>O and CO equal within uncertainty (as the amount of oxidation in a H<sub>2</sub>O-  
181 feed half cycle must equal the reduction in a CO-feed half cycle), and both in excess of 75%;  
182  $K^*$  is observed to have a value of approximately 14 (Region B of Fig. 2a, Fig. 2b and  
183 Supplementary Fig. 7). It is quite clear that equilibrium limitations ( $K^* = 1$ ) have been  
184 overcome. Furthermore, the behaviour of the reactor was modelled by assuming plug-flow in  
185 the gas phase and gas-solid equilibrium with no adjustable parameters (Supplementary  
186 Information Section 7). Fig. 2c shows the outlet mole fractions versus time from the model.  
187 Good agreement is seen with Fig. 2b and similar conversions and value of  $K^*$  are predicted.  
188 By simple valve switching our reactor produces the pure, separated H<sub>2</sub> and CO<sub>2</sub> products of  
189 Reaction 1 from different ends of the bed.

190 Spatially- and temporally-resolved powder x-ray diffraction was used to investigate the state  
191 of the LSF oxygen-carrier material during reactor operation (there was no evidence for the  
192 formation of any additional phases during operation). Shifts in 2 $\theta$  peak positions (Fig. 3a,  
193 Supplementary Fig. 3 and more discussion in Supplementary Information Section 4) were  
194 used to determine changes in lattice parameter which, with calculated chemical and thermal  
195 expansion coefficients and a defect chemistry model (Supplementary Information Section 1),

were used to calculate the oxygen content of the material as a function of position in the bed immediately after oxidation and reduction half cycles (Fig. 3b). It is evident that a profile in the oxidation state of the non-stoichiometric material has developed as predicted. Furthermore, although the degree of oxidation of the OCM increases after bed oxidation at every location investigated in the bed compared to immediately after bed reduction, it is clear that the bed retains an oxidation state profile throughout.

To test the concept of chemical memory further we predict that we can improve the memory of the bed and improve conversions by shortening the half-cycle durations (less oxygen is removed and added in each cycle). Thus we see in Fig. 2c, that when the half-cycle duration is reduced from 60 seconds to 48 seconds both conversions increase from in excess of 75% to in excess of 80%, and  $K^*$  doubles from 14 to 28. When the duration increases, Fig. 2d, we expect a loss of memory and we see that a 120-second duration results in a decrease of conversions to barely more than 50%;  $K^*$  decreases to 1.4. This dependence of  $K^*$  on half-cycle duration is also confirmed by use of the thermodynamic model of the reactor (Fig. 2e, Fig. 2f, Fig. 2g). The model predicts values of  $K^*$  in Regions B, C and D of 13, 41 and 1.35 compared to the experimentally obtained values of 14, 28 and 1.4. Thus it appears that the reactor does not suffer from significant kinetic limitations. Furthermore, we may use a reactor bed with a fully developed oxidation state profile for the reverse water-gas shift reaction (Supplementary Fig. 9). By feeding  $H_2$  to the reduced end of the bed and  $CO_2$  to the oxidised end we instantly achieve conversions in excess of equilibrium limitations. Such facile switching between forward and reverse reactions is unique to a reversibly-operated chemical memory reactor.

## Discussion

The hydrogen produced by the reactor is free of carbon monoxide as no carbon is carried over from the reduction cycle to the hydrogen production cycle. This addresses a key challenge in hydrogen production. Furthermore, because of a lack of equilibrium limitations, the exothermic reaction can be performed at high temperature (taking a high temperature feed from a reforming or gasification process) and thus capitalise on the high kinetic rates available, even in the absence of a shift catalyst. So, whereas conventional hydrogen production requires two reactors (a high and a low temperature shift reactor) to drop carbon monoxide mole fractions to reasonable levels and then a separation step to remove carbon dioxide from the hydrogen, our reactor accomplishes all of these steps in one unit and has kinetics that are more favourable than a conventional process. This, if applied practically, could lead to significantly reduced hydrogen-production process footprints and costs. We must also note that the OCM is stable over a larger number of cycles. 300 cycles were performed with no measurable deterioration in  $K^*$  (Supplementary Fig. 7) or change in OCM morphology (Supplementary Fig. 8). The origin of the OCM stability presumably results from the ability of the OCM to donate and receive oxygen without a phase change.

It may be possible to implement more complex reaction schemes involving the introduction of methane (or natural gas) as the reducing feed. Internal reforming of the methane with lattice oxygen from the OCM would result in syngas formation. It would be possible to operate such a reactor in a number of modes optimised for e.g. combined syngas and hydrogen production or hydrogen production alone. Depending on the application area more than two feeds could be desirable with the use of, e.g., an air feed to ensure an overall autothermal process if reforming a hydrocarbon feed. This raises the possibility of using single reactors, albeit dynamically operated, for the conversion of natural gas to hydrogen.

It must be noted that the ‘memory reactor’ concept developed here does not only apply to oxygen exchange reactions. Materials with non-stoichiometry in, e.g., hydrogen also

exist. It may be possible to apply such materials to reversibly couple hydrogenation and dehydrogenation reactions. This application could be crucial if chemical hydrogen storage becomes more important as one would be able to regenerate hydrogen at its supply pressure without significant energy input.

## **Methods**

### **Material synthesis**

$\text{La}_{0.6}\text{Sr}_{0.4}\text{FeO}_3$  was synthesised via the sol-gel method using stoichiometric ratios of  $\text{Fe}(\text{NO}_3)_3(\text{H}_2\text{O})_9$  (Sigma Aldrich 216828),  $\text{La}(\text{NO}_3)_3(\text{H}_2\text{O})_6$  (Sigma Aldrich 61520), and  $\text{Sr}(\text{NO}_3)_2$  (Sigma Aldrich 243426) mixed with citric acid (Sigma Aldrich 791725) and ethylene glycol (Sigma Aldrich 324558) in molar ratios to the total cations present of 1:1 and 1.2:1 respectively. The total cation quantity was chosen to make 100 g of  $\text{La}_{0.6}\text{Sr}_{0.4}\text{FeO}_3$ . 450 mL of deionised  $\text{H}_2\text{O}$  was added and the solution was stirred, decanted into a 10 L beaker and dried at 60°C for 48 hours. The resulting orange cake was lightly crushed and placed in a covered 700 mL alumina high form crucible and heated to 1050°C at 1°C min<sup>-1</sup> and held for 18 hours. The resulting powder was then sieved to select particle sizes between 80 and 160  $\mu\text{m}$ .

### **Flow system and reference experiments**

The flow system (Supplementary Fig. 2) employed 4-way cross-over valves to switch the gas composition being fed to the fixed-bed reactor, switch direction of feed to the reactor and to maintain continuous flow through the reactor and the gas analysis equipment. One complete redox cycle contained six phases, two phases of reactive gas feed of CO or  $\text{H}_2\text{O}$  and four

phases with an inert (argon) feed. The directional change of the feed to the reactor was always performed during an inert feed.

The system was operated with a furnace set point of 820°C in a vertical orientation for the *operando* x-ray diffraction studies on ID22 at ESRF and in a horizontal orientation for a long-term stability experiment (Supplementary Fig. 7), the reverse WGS experiment (Supplementary Fig. 9) and two further reference experiments involving a conventional mixed-reactant WGS experiment and an empty reactor with unmixed reactants (Supplementary Fig. 10). All total flows were set (unless otherwise stated) to  $3.4 \times 10^{-5} \text{ mol s}^{-1}$  (50 ml min<sup>-1</sup> at NTP).

### ***Operando* XRD setup**

The *operando* XRD reactor bed was held in a vertical furnace at a nominal 820°C and consisted of LSF641 powder, 1.43 g ( $6.43 \times 10^{-3} \text{ mol}$ ), packed into a quartz tube with an internal diameter of 4 mm with 2 mm wall thickness to form a fixed-bed reactor that was 114.5 mm long. Local temperature was recorded with a K-type thermocouple placed in contact with the reactor tube which was allowed to equilibrate over 10 minutes. The local temperature was found to be 790°C at the bottom of the reactor bed, 810°C in the middle and 820°C at the top. This leads to a thermally-induced variation of oxygen content in the absence of reaction which is accounted for in our analysis.

*Operando* X-ray powder diffraction was conducted at the high-resolution powder diffraction beamline ID22 at ESRF (MA2914) using the multi-analyser stage<sup>25</sup>. The energy used was 38 keV. The multi-analyser stage is composed of nine Si 111 analyser crystals preceding nine scintillator detectors, the detector channels being 2 degrees apart. The 2 $\theta$  arm was scanned from 9 to 11.2 degrees (2 $\theta$ ) at a speed of 4 degrees min<sup>-1</sup>. This setup yielded a

total effective scan range of 1 to 19.2 degrees, binned to 0.002 degree resolution, with 0.2 degree overlap between each detector. The effective scan time was 36 seconds when initialisation of the positioner at the beginning of each scan was taken into account.

#### Data availability statement

Data supporting this publication is openly available under an “Open Data Commons Open Database License”. The data with additional metadata are available at <http://dx.doi.org/10.17634/080913-1>

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375

## 376 **Author contributions**

377 ISM conceived the overall idea, secured funding, and managed the work. ISM, JSOE wrote  
378 the main text. ISM, BR, WH, CdL, JSOE were responsible for the data analysis, modelling  
379 and interpretation. BR, CD, CdL, CD, FGG, CM, EIP, CRT, performed the experiments.

380

## 381 **Competing interests**

382 The authors declare no competing interests.

383

## 384 **Additional information**

385 Supplementary Information is linked to the online version of the paper at  
386 [www.nature.com/nchem/](http://www.nature.com/nchem/).

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## 393 **List of figure captions**

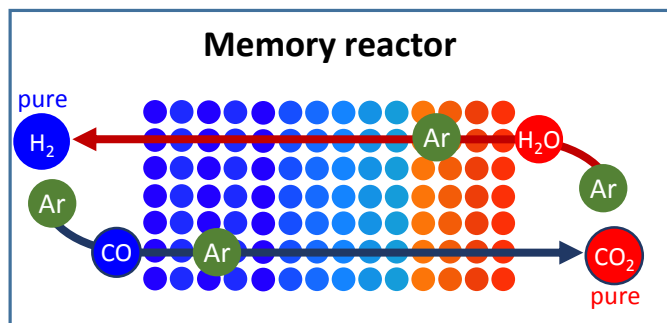
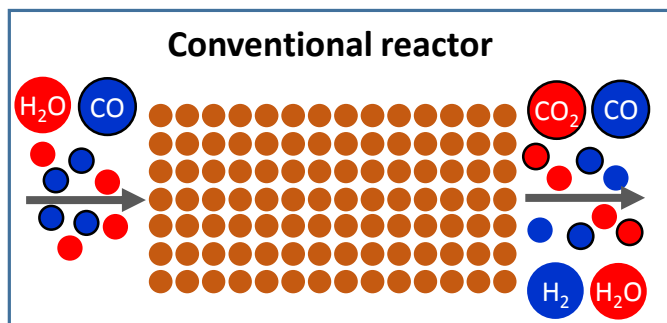
394 **Fig. 1. Thermodynamic reversibility in a water-gas shift reactor.** Colour coding of  
395 oxygen chemical potentials in the gas phase and oxygen content in the solid phase (red to  
396 blue for oxidising to reducing) is used to show that within conventional mixed gas reactors  
397 and metal-metal oxide chemical looping reactors the reactants cannot be fully converted. **(a)**  
398 Conventional WGS reactor producing a mixture of reactants and products. **(b)** Equilibrium  
399 relationship for a metal-metal oxide showing solid-phase oxygen content versus oxygen  
400 chemical potential of the gas phase. Note that only orange and light blue potentials are  
401 required to show where the phase transition lies. **(c)** The use of such a metal-metal oxide  
402 OCM for H<sub>2</sub> production in a chemical looping cycle where water is fed over the metal. The  
403 phase transition is not sufficiently reducing to produce a high mole fraction of H<sub>2</sub>. **(d)**  
404 Reduction of the metal oxide (CO is fed from the opposite end of the bed to H<sub>2</sub>O) cannot  
405 produce a high mole fraction of CO<sub>2</sub>. **(e)** The mode of operation of our memory reactor. The  
406 reactor contains a non-stoichiometric oxygen carrier (e.g. a perovskite, ABO<sub>3-δ</sub>) and operates  
407 under reverse flow with feeds of 5% CO (during the reduction step) and 5% H<sub>2</sub>O (during the  
408 oxidation step). The reactive stages are preceded and followed by a flow of argon. **(f)**  
409 Equilibrium relationship for a non-stoichiometric oxide showing solid-phase oxygen content  
410 versus gas phase oxygen chemical potential. Note that oxygen capacity is available over the  
411 entire range of oxygen chemical potentials. **(g and h)** A non-stoichiometric oxide develops a  
412 profile of oxidation states along the bed allowing the production of pure products if cycle  
413 durations do not remove the profile from the bed. **(g)** A H<sub>2</sub>O feed is converted almost  
414 entirely to H<sub>2</sub> as the H<sub>2</sub> exits over the reduced end of the bed before **(h)** switching the  
415 direction of flow and converting CO almost entirely to CO<sub>2</sub> as the CO<sub>2</sub> exits over the oxidised  
416 end of the bed. More explanation of the reactor concept can be found elsewhere  
417 (Supplementary Video 1).



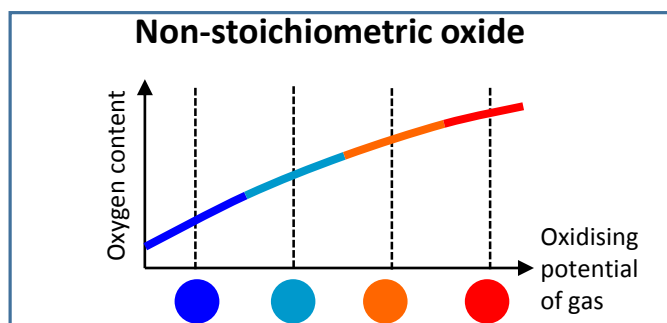
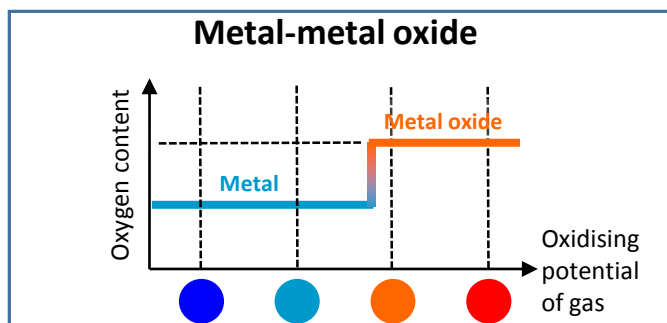
**Fig. 2. Conversion, reactor performance measure ( $K^*$ ) and outlet mole fractions (real and modelled) versus cycle number show that equilibrium limitations have been overcome.** (a) Time-averaged conversions of CO ( $\bar{x}_{CO}$ , squares) and H<sub>2</sub>O ( $\bar{x}_{H_2O}$ , triangles) on the left axis and reactor performance measure,  $K^*$ , on the right axis, as a function of cycle number for a reverse-flow memory reactor containing non-stoichiometric La<sub>0.6</sub>Sr<sub>0.4</sub>FeO<sub>3- $\delta$</sub> . Region A (evolution of the oxidation state profile) (Cycles 1-15) with 60-second feeds of CO and H<sub>2</sub>O, Region B (Cycles 16-30) with 60-second feeds, Region C (Cycles 31-45) with 48-second feeds, and Region D (Cycles 46-60) with 120-second feeds. The dashed lines are equivalence lines between an overall conversion and the corresponding measure of reactor performance. Note, that the  $K^*$  for Cycle 46 is 0.7 and is off-scale. The small difference between the conversions of CO and H<sub>2</sub>O are due to small differences in the flowrates between oxidising and reducing half cycles; the oxygen balance closes to within 97%. (b), (c) and (d) Measured effluent gas mole fractions versus time for representative cycles. (e), (f) and (g) Corresponding modelled effluent gas mole fractions versus time.

**Fig. 3. Representative shifts in 2 $\theta$  peak positions and local oxygen content of the La<sub>0.6</sub>Sr<sub>0.4</sub>FeO<sub>3- $\delta$</sub>  versus reactor position showing changes in lattice parameter and oxygen content are a function of axial position.** (a) *Operando* XRD scans, arbitrary intensity, from the H<sub>2</sub>O-feed end of the reactor bed after the CO feed of Cycle 22 (red triangles) and the H<sub>2</sub>O feed of Cycle 23 (blue squares) showing the lower 2 $\theta$  peak positions and thus larger cubic lattice parameter after CO feed compared to H<sub>2</sub>O feed. (b) Local oxygen content of the non-stoichiometric solid (La<sub>0.6</sub>Sr<sub>0.4</sub>FeO<sub>3- $\delta$</sub> ), 3- $\delta$ , relative to the local oxygen content of the reactor bed in the absence of chemical reaction, 3- $\delta^*$ , versus reactor position, for Region B in Fig. 2, immediately after oxidation (red triangles) and reduction (blue squares). The CO-feed end of the reactor remained the most reduced location (lowest oxygen content) and the H<sub>2</sub>O-feed end of the reactor the most oxidised (highest oxygen content). There is a profile in oxygen content which, although shifted, from oxidation to reduction, retains a memory of the gas feeds.

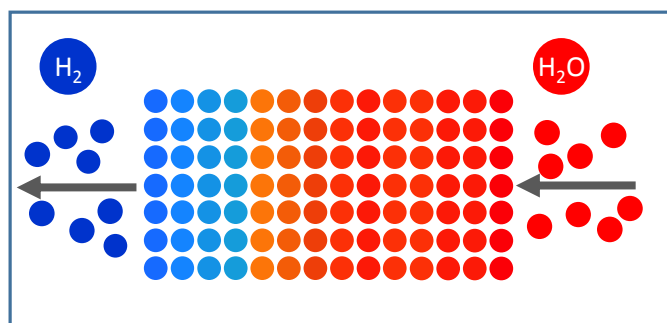
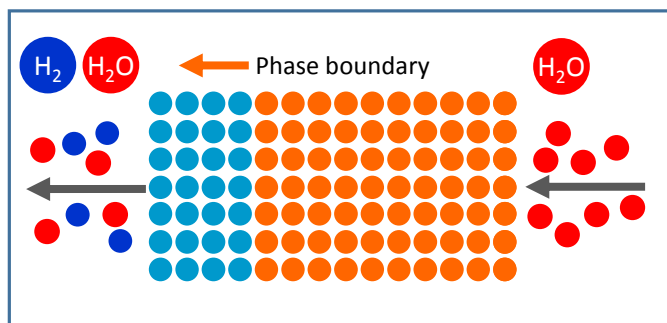
a



b



c



d

